



Nature and photoreactivity of TiO₂-rGO nanocomposites in aqueous suspensions under UV-A irradiation

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ABSTRACT

Different studies to unravel the nature of the activity of TiO₂ photocatalysts modified with rGO were carried out. The band edge potentials and the band gap energy of the nanocomposites were determined by performing electrochemical impedance and UV–vis diffuse reflectance measurements, respectively. However, no changes were observed when TiO₂ is modified with rGO. Nevertheless, the presence of rGO in the hybrid composite led to a low charge transfer resistance across the electrode-electrolyte interface, observing even a tenfold increase in the photocurrent values in methanol photo-oxidation for P25-rGO 1%. Moreover, a higher oxygen reduction current was found when increasing the rGO concentration that could lead to a higher ROS formation. In order to analyze the beneficial properties of the hybrid materials, the influence of rGO doping ratio on oxalic acid photocatalytic degradation and on oxalic acid adsorption onto the nanocomposites surface was studied, both of them under UV-A light irradiation. In addition, the photoactivity of the conduction band electrons and the valence band holes was investigated by performing EPR and transient absorption spectroscopy measurements under UV-A illumination in O₂ or N₂ atmospheres. It was demonstrated that rGO behaved as an electron acceptor. Finally, TAS results under O₂ and N₂ atmospheres proved that the role played by rGO was not as crucial in excess of dissolved O₂ as in N₂ atmosphere. These findings agree with the observed photocatalytic activity and EPR measurements. Nevertheless, generation of HO[•] in N₂ saturated suspensions was highly increased with the addition of rGO.

1. Introduction

Photocatalytic Advanced Oxidation Process (AOP) based on semiconductors have emerged as a promising technology for water treatment [1]. The increasing interest is related to the ability of semiconductors to generate reactive electron-hole pairs when illuminated with light of energy greater than their band gap. These photogenerated charge carriers are able to form highly reactive chemical species, such as hydroxyl radicals HO[•], which allow disinfecting water and/or degrading highly recalcitrant pollutants present in aqueous systems [2–4].

Because of the high band gap value and the low photonic efficiency exhibited by TiO₂, a great deal of attention has been focused on the synthesis of new hybrid materials lacking these limitations [5–8]. Graphene- and graphene-derivative-based TiO₂ have been proposed as

highly photoactive nanocomposites due to their unique properties, such as large specific surface area and high electrical conductivity [9–14]. Furthermore, the photoactivity is enhanced on account of the fact that graphene oxide (GO) and reduced graphene oxide (rGO) absorb light in the UV–vis wavelength region, leading to the formation of reactive oxygen species [2,12,13].

Unfortunately, no consensus has been completely established so far about the role of rGO during the photocatalytic treatment of pollutants dissolved in water. Minella et al. [15] proposed a mechanism of underlying reactions in the presence of TiO₂-rGO composites. The role played by rGO appears to depend on the adsorption and the light absorption properties of the substrate. Thus, only when the adsorption of the organic probe compound is significant, the electron transfer from the two phases can occur. This evinces the necessity to deepen into the

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understanding of the underlying mechanism. However, to evaluate the right development of the photocatalysts and the influence of their improved properties on the photocatalytic activity, the knowledge of the energetic position of the conduction and valence band edges and the reaction mechanism itself is crucial.

In this study, the nature of the activity of a TiO₂ photocatalyst modified with rGO synthesized by a hydrothermal method was investigated. Different rGO doping ratios were analyzed in the photodegradation of oxalic acid under UV-A light irradiation. In order to obtain a better knowledge about the origin and mechanism of the observed photoactivity, oxalic acid photodegradation runs were carried out. The actual position of the band edges and the band gap energy were determined by performing electrochemical impedance spectroscopy and UV–vis diffuse reflectance, respectively. Furthermore, electrochemical impedance spectroscopy and photocurrent response measurements were carried out to study the charge separation of the photo-generated charge carriers. Additionally, the reduction pathways of oxygen were investigated by measuring the oxygen reduction current at different potentials. Finally, EPR and transient absorption spectroscopy (TAS) experiments were performed to investigate the conduction band electrons and the valence band holes activity under UV-A illumination under O₂ or N₂ atmospheres. These results were related to the performance observed in the oxalic acid oxidation reactions.

2. Experimental section

2.1. Materials

Graphene oxide (GO) water dispersions (0.4 wt% Concentration) were purchased from Graphenea company. The GO used had a monolayer content over 95%, a particle size of 600 nm (DSL) and the following elemental analysis data was obtained: C = 49–56%, H = 0–1%, N = 0–1%, S = 2–4%, O = 41–50%. Titanium dioxide P25 Aeroxide® (80:20 anatase-rutile, BET specific surface area 54 m²/g, average anatase and rutile crystal size of 21 and 33 nm, respectively) was provided by Evonik Company. The spin trap 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), oxalic acid (OA) (≥ 99%), FTO (fluorine-doped tin oxide SnO₂:F) glass and Dimethyl Sulfoxide (DMSO) were purchased from Sigma-Aldrich.

Deionized water (H₂O) was supplied from a Millipore Milli-Q system with a resistivity equal to 18.2 MΩ cm. pH adjustments and measurements were performed using KOH provided by PanReac AppliChem. All the chemicals were used as received without further purification.

2.2. Synthesis of P25-rGO

P25-rGO composites were prepared by a hydrothermal method. To sum up, 2 g of P25 were suspended in 400 mL of deionized water and dispersed for 1 h using a 100 MHz tip (Misonix Microson 2000XL). Subsequently, the desired amount of GO was added to the suspension and sonicated for another hour to achieve a good dispersion of GO sheets in a homogenous medium. Subsequent to sonication, the mixture was transferred to a 600-mL Teflon-lined stainless steel autoclave reactor and subjected to hydrothermal treatment overnight at 120 °C. After that, the composite was collected by centrifugation and dried at 60 °C. The weight ratio P25: rGO was 0, 0.1, 0.5 and 1%, called along the paper as P25-rGO 0%, P25-rGO 0.1%, P25-rGO 0.5% and P25-rGO 1%, respectively.

2.3. Photocatalyst characterization

Diffuse reflectance spectra were recorded with a UV–vis Varian, Cary 100 Bio UV–vis, equipped with an integrating sphere. Analyses of the band gap transitions of the samples were made using the Kubelka-Munk radiative transfer model and the Tauc plots [16]. An indirect allowed transition was considered to calculate the band gap energies

[17,18]. Raman spectrum was recorded on a Renishaw Micro Raman spectrometer ($\lambda = 532$ nm) equipped with a 20 mW He-Ne laser emitting at 532 nm. The spectra were recorded using 0.2 mW of incident power, 5 repetitions and 10 s of acquisition time.

Catalysts structural characterization were performed with a X-ray polycrystal PANalytical X'Pert PRO using nickel-filtered Cu K α (1.541874 Å) radiation operating at 40 kV and 40 mA, with a 0.02° step size and accumulating a total of 50 s per point. Crystallite sizes was estimated by employing the Scherrer equation [19] and the crystalline phases were identified by comparison with ICDD PDF database [20]. The quantification of each previously selected crystalline phase was automatically calculated by X'Pert Highscore Plus software by the RIR (Reference Intensity Ratio) method.

Scanning electron microscopy (SEM) analyses were performed to determine morphology of the studied TiO₂ powders (Philips XL 30 S-FEG). Transmission Electron Microscope study of the composites was carried out in a field emission gun JEOL 2100 F microscope operating at 200 kV. Specimens for Transmission electron microscopy were prepared by dry deposition of the composites in a lacey carbon copper grid.

Transient absorption spectroscopy (TAS), described previously in more detail [21], was carried out using an Applied Photophysics LKS 80 Laser Flash Photolysis Spectrometer. The proper diffuse reflectance accessory was used to measure in diffuse reflectance mode. The samples were excited by an Nd-YAG laser (Quantel; Brilliant B; 3rd harmonic, 355 nm) and light up by a pulsed xenon lamp (Osram XBO; 150 W) to analyze light absorption of the photogenerated transient species. Afterwards, the diffusely reflected light was led to the monochromator and detector (Hamamatsu PMT R928). For all the experiments excitations energy densities of 2.2 mJ cm⁻² per pulse were used, monitored by a Maestro energy meter (Gentec-EO). A 100 Ω value was always used as terminal resistance and the number of averages was 12 shots. All the samples were dry powder placed into a quartz flat cuvette and they were flushed with nitrogen or oxygen for more than 30 min before performing the measurements. To analyze the results obtained, the reflectance changes ΔJ of the samples were obtained from the absorbance:

$$\Delta J = 1 - 10^{-Abs} = \frac{I_0 - I}{I_0} \quad (1)$$

Where ΔJ can be correlated with the transient absorption of the photogenerated species and I_0 and I are the intensities of the reflected light before and after the laser pulse, respectively.

2.4. Electrochemical characterization

The photo-anodes of the synthesized photocatalysts were prepared by following the screen-printing method [22]. The detailed procedure is described in detail in the Supplementary Information: Procedure to prepare the photo-anodes by the screen-printing method.

The measurements were carried out with a three compartment cell consisting of a working (photo-) electrode (WE), a Pt wire counter electrode (CE) and an Ag/AgCl/KCl (3 M) reference electrode (RE). All potential values presented herein are pH-corrected and expressed vs. RHE (reversible hydrogen electrode). The photo-response of the prepared films was tested under chopped light irradiation at a constant potential 0.8 V vs. RHE by a Zennium potentiostat and a PECC-2 photoelectrochemical cell (Zahner-Elektrik GmbH & Co. KG). The illumination source, a 300 W Xe lamp with an AM 1.5-global filter providing an intensity of 680 W m⁻² in the regime of 280–1000 nm (LOT-Quantum Design GmbH), was chopped on and off with a frequency of 300 mHz. Regarding the electrolyte, a 0.1 M Na₂SO₄ aqueous solution with 10% v/v CH₃OH was used.

For the rest of electrochemical experiments a 0.1 M Na₂SO₄ aqueous solution was used as the electrolyte. The electrochemical impedance spectroscopies (EIS) of the as-prepared samples were carried out within a frequency range from 0.1 Hz to 30,000 Hz and the applied bias was

-0.0 V vs. RHE. The flat-band potentials (V_{fb}) were determined from Mott–Schottky plots by Impedance spectra collected in the potential range of +1 to 0.2 V vs. RHE with a step width of -25 mV. Each spectrum was recorded at a fixed potential in the frequency range of 0.1 to 30,000 Hz with 10 steps per decade. A Randles circuit was used to fit the spectra to obtain the value of the space charge layer capacitance (C_{sc}) at each potential. Rather than ordinary capacitance, constant phase elements (CPE) were used. In this work the flat-band potentials of the photo-anodes were calculated from the resulting Mott–Schottky plots (C^{-2} vs. applied potential). The extrapolation of the linear trend in the Mott–Schottky plot to the x-axis (potential) enables to calculate the V_{fb} for a given semiconductor oxide [8,16].

Oxygen reduction currents were obtained by performing linear sweep voltammetry both in nitrogen or oxygen-saturated electrolytic solutions in +0.8 V to -0.1 V potential range vs. RHE with a step width of 10 mV and a scan rate of 1 mV s⁻¹. The difference between both scans constitutes the oxygen reduction current.

2.5. ATR-FTIR adsorption and photocatalytic experiments

The photocatalyst layer was performed following the procedure described in [23,24] and is summarized in the Supplementary Information: Deposition of the TiO₂-rGO layer on the ATR crystal. Prior to starting, an infrared spectrum of the P25-rGO film was taken as a background. Two groups of blank reference spectra in the dark and under irradiation were obtained by adding 3 mL of Milli-Q water to the cell. Then, the sample was allowed to equilibrate with the water for 45 min in the dark and infrared spectra were recorded every 300 s. When the last spectrum was collected, the film was irradiated with UV-A light and a new set of spectra were collected every 300 s for 2 h. Right after both groups of blank spectra were recorded, the water was replaced by 3 mL of a 1 mM oxalic acid (OA) solution at pH 5 adjusted by adding KOH. Two new groups of spectra were monitored in the dark and under UV-A light irradiation. The final spectra were obtained by subtracting the corresponding blank. FTIR spectra were collected at room temperature using a FTIR spectrometer (IFS 66 BRUKER) equipped with an internal reflection element 45° ZnSe crystal and a deuterated triglycine sulphate (DTGS) detector. The interferometer and the infrared light path in the spectrometer were constantly purged with Argon to avoid H₂O and CO₂ contamination. Spectra were recorded in the 1800–1200 cm⁻¹ region, employing a resolution of 4 cm⁻¹ and an averaging of 300 scans.

The samples were irradiated with UV-A light using a LED lamp (Model LED-Driver, THORLABS) emitting 365 nm UV light (FWHM = 7.5 nm). The lamp was placed at a distance of ca. 30 cm from the surface of the test solution to achieve an intensity of UV-A light of 1.0 mW cm⁻², measured by an UV radiometer (Dr. Hönle GmbH, Martinsried, Germany).

2.6. Photocatalytic activity

The photocatalytic degradation measurements were carried out using a 0.25 L semi-continuous cylindrical reactor made of borosilicate glass and placed under four fluorescent lamps (PHILIPS CLEO 15 W, 365 nm, FWHM = 20 nm) used as an irradiation source. The distance to the lamps from the reactor was adjusted so that the average UV-A flux value was 1.08 mW cm⁻² measured by an UV-A radiometer (LT Lutron UVA Light Meter). The photoreactor was filled with 200 mL of a suspension with 0.20 g L⁻¹ of the hybrid photocatalysts and 1 mM of oxalic acid at pH 5 adjusted by adding KOH. The photocatalytic reactions were performed at room temperature (25–30 °C) and atmospheric pressure. The mixture was continually agitated while bubbling air using an air pump (Elite 801, 1000 cm³ min⁻¹). Prior to reaction, the mixture was premixed for 4 h in darkness to allow adsorption equilibrium to be reached. Samples were taken out every 15 min to follow the reaction and filtered using 0.2 µm-pore-size PTFE syringe filters.

High Performance Ionic Chromatography, HPIC, was used to identify and quantify oxalic acid concentration in a DIONEX ICS-1000 with a conductivity detector and an electro-regenerator-suppressor. An Ion Pac AS9-HC 2 × 250 mm and a guard column Ion Pac AG9-HC 2 × 50 mm from DIONEX was used. The eluent was an alkaline solution of 8·10⁻³ mol L⁻¹ Na₂CO₃ and 1.5·10⁻³ mol L⁻¹ NaHCO₃. The temperature of the detector conductivity cell was kept constant at 35 °C.

2.7. EPR study

Generation of hydroxyl radical and superoxide radical anions upon UV light irradiation of the synthesized P25-rGO photocatalysts was examined by measuring the EPR signal of the DMPO–HO· and DMPO–O₂^{·-} species, respectively. EPR spectra were recorded at room temperature on a MiniScope X-band EPR spectrometer (MS400 Magnetech GmbH, Germany) operating at 9.43 GHz field modulation. The acquisition parameters to detect DMPO–HO· / DMPO–O₂^{·-} were as follows: center field: 339 m T, sweep width: 8/6 m T, sweep time: 25/15 s, number of scan: 1, modulation amplitude: 0.1 m T, power: 10 mW, gain: 5. The experimental EPR spectra acquisition and simulation were carried out using MiniScope and Winsim 2002 software. For the sample preparation, the photocatalyst (1 g L⁻¹) was suspended in water or DMSO to detect DMPO–HO· or DMPO–O₂^{·-}, respectively, and the suspension were subsequently dispersed by using an ultrasonic bath. Prior to the measurement, 1 mL of the suspension was introduced into the Eppendorf tube and then 200 µL of 40 mM of DMPO were immediately added. The tube was shaken by hand to homogenize the sample. The suspensions were transferred immediately to 50 µL borosilicate capillaries (Hirschmann ringcaps). The samples were irradiated directly in the EPR spectrometer microwave cavity by a spot UV-light (LC8, Hamamatsu, 200 W super-quiet mercury-xenon lamp) through the quartz window of the cell.

3. Results and discussion

3.1. Characterization of P25-rGO composites

In order to confirm the TiO₂ modification with rGO and to characterize the crystal structure of the carbon materials Raman spectroscopy was applied. Fig. 1 shows the Raman spectra of GO and of P25-rGO nanohybrid materials with different rGO mass doping ratio. All the TiO₂ based samples exhibited four different peaks corresponding to the vibration modes of anatase located at 145 cm⁻¹ (E_g), 396 cm⁻¹ (B_{1g}), 517 cm⁻¹ ($B_{1g} + A_{1g}$), and 638 cm⁻¹ (E_g) [6,25]. As for GO, two

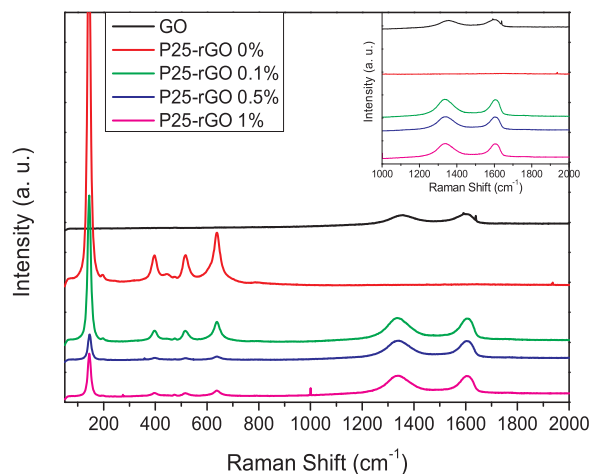


Fig. 1. Raman spectra of GO, P25-rGO 0%, P25-rGO 0.1%, P25-rGO 0.5%, and P25-rGO 1%; and the magnified spectra ranging from 1000 cm⁻¹ to 2000 cm⁻¹ (upper right).

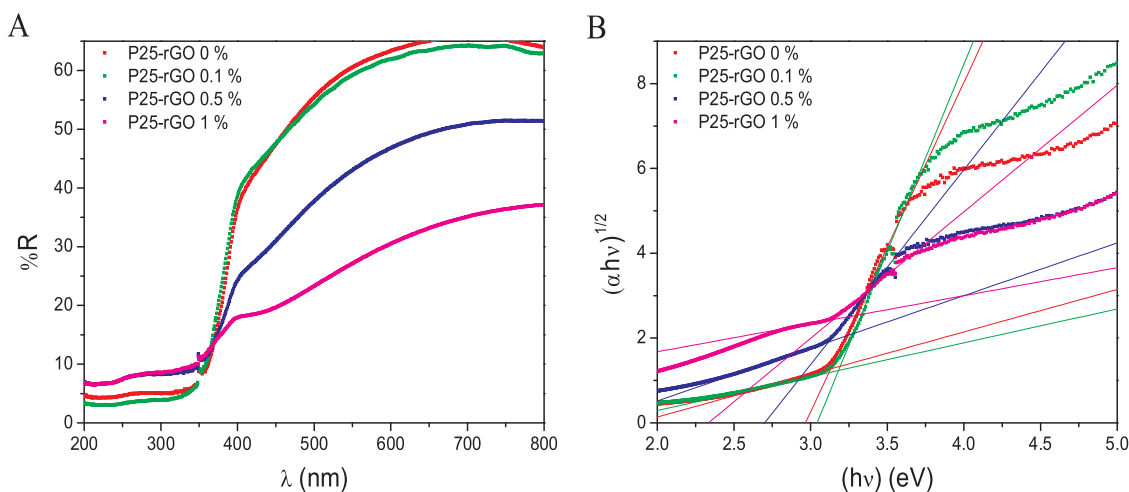


Fig. 2. Diffuse reflectance UV–vis spectra of P25-rGO composites (A) and Tauc plots (B) used to estimate the band gap values. α represents the absorption coefficient.

different peaks ascribed to the D band and to the G band were observed at 1340 and 1605 cm^{-1} , respectively. These two bands were also present in the Raman spectrum of the composites, proving the presence of rGO. Whereas the D peak is attributed to internal structural defects, edge defects or dangling defects caused by the existence of different oxygen-containing functional groups in the case of GO, the G peak is ascribed to C–C and C=C bonds [2,26]. Hence, a narrow G peak indicates a low amount of functional groups. The area under both peaks was calculated and the ratio A_D/A_G was compared. While GO yielded an A_D/A_G value close to 1.13, indicating a disordered structure [6,27], values of 1.44, 1.44 and 1.37 were estimated for P25-rGO 0.1%, P25-rGO 0.5%, and P25-rGO 1%, respectively. The ratio between the areas of both peaks increases as a consequence of the strong interaction between TiO_2 and rGO sheets, giving rise to a higher disorder degree and suggesting the reduction of GO and the contribution of remaining oxygenated functional groups [6,7,25,28].

To further study the interaction between TiO_2 and rGO and their effect on the light absorption, diffuse reflectance UV–vis spectroscopy measurements were conducted. Fig. 2A and B show the diffuse reflectance spectra of the different P25-rGO films and the Tauc plots, respectively. When the absorption spectra of the samples are evaluated, it could be noted that the higher the rGO content, the higher the absorption in the visible light range. The optical band gap energy of the samples was determined through the Tauc plots. Optical band gap values of 3.1 eV were found for pure TiO_2 , P25-rGO 0.1%, P25-rGO 0.5% and P25-rGO 1%, respectively, which indicates that the band gap energy remained unchanged by the introduction of rGO. So, as a result the variation is negligible and modification of TiO_2 with rGO does not show a reduction of the band gap energy [15,25].

The XRD patterns of pure GO and P25-rGO composites are shown in Fig. S1. Although of GO exhibited a strong diffraction peak at 11° , this peak was not observed for any of the P25-rGO nanocomposites, which consisted of the characteristic peaks of anatase and rutile crystalline phases. This could be explained because of the reduction of GO to rGO and the relatively low amount and intensity of rGO/GO compared to the peaks of TiO_2 [7,14,29].

To analyze the morphology and structure of the photocatalysts SEM and TEM were used. Some images of P25-rGO 0%, P25-rGO 0.5% and P25-rGO 1% can be seen in Fig. 3. From Fig. 3A and B it can be noted that primary particles have uniform shape and size for both samples. These primary particles were observed to be densely agglomerated. In Fig. 3B an rGO sheet loaded with TiO_2 particles could be detected. A detailed insight into the microstructure of the P25-rGO 1% agglomerates is shown in the TEM micrograph of Fig. 3C. The picture exhibits TiO_2 particles with a size ranging between 15 and 40 nm. The presence of graphene oxide is also evident in some areas. Through HRTEM we

have located regions where the TiO_2 particles appear surrounded by some sheets of graphene oxide as can be seen in Fig. 3D. The picture displays at least two or three particles surrounded by a wrinkled graphene sheet (Marked with red arrows). Fig. 3E displays one of these particles at higher magnifications. As can be deduced from its FFT (Fast Fourier Transform, Fig. 3F) the particle is oriented along the [111] zone axis of the anatase phase. Although the partially reduced graphene oxide is recovering part of the particles, it also seems to interconnect them proving an intimate contact between TiO_2 and rGO that should improve electron transfer from the photo-excited TiO_2 to rGO.

One of the most significant properties of semiconductors is the absolute position of the conduction and valence band edges as the possibility of an electron transfer to take place depends on the band potentials. In order to know whether the coexistence of TiO_2 and rGO may shift the band position, electrochemical impedance spectroscopy experiments were carried out at different potentials. Values of the space charge layer capacitance (C_{sc}) were derived by fitting the impedance spectra at each potential to a Randles circuit. The value of exponential parameter of the CPE was found to be between 0.9 and 1.0. Afterwards, Mott-Schottky plots were constructed by depicting the inverse square of the C_{sc} per unit of area against the respective applied potential (Fig. 4). Mott-Schottky plots showed a linear regimen which could be extrapolated to the x axis to obtain the flat-band potential (E_{FB}) [8,16]. By the slope of the plots it was determined that the studied photocatalysts are n-type semiconductors [16]. The flat-band potentials of P25-rGO 0%, P25-rGO 0.5% and P25-rGO 1% were -0.28, -0.27, and -0.29 V vs. RHE respectively. Therefore, as expected, no shift of the E_{FB} was observed when TiO_2 was modified with rGO. It is generally known that the conduction band edge (E_{CB}) of an n-type semiconductor is around 0–0.2 V more negative than the E_{FB} [30–32]. In this study a value of 0.1 V was chosen and the estimated conduction band potentials for P25-rGO 0%, P25-rGO 0.5%, and P25-rGO 1% were -0.38, -0.37, and -0.39 V vs. RHE, respectively. Taking into account the value of the band gap energies obtained from optical spectroscopy, the values of the valence band potentials were also estimated (2.76 V, 2.75 V, and 2.75 V vs. RHE for P25-rGO 0%, P25-rGO 0.5%, and P25-rGO 1%, respectively).

To understand the difference in the electronic properties of pure TiO_2 and rGO modified titania, the photocurrent response was measured as it provides useful information about the generation and separation of the photogenerated electron-hole pairs under irradiation [7,33]. Fig. 5 illustrates the photocurrent response of the films at 0.8 V bias potential vs. RHE in a 0.1 M Na_2SO_4 aqueous solution containing 10% v/v CH_3OH under chopped UV–vis irradiation (A) and visible irradiation ($\lambda > 450$ nm) (B). In both figures, it can be noted that the photocurrent responses promptly decrease when the light is switch off and comes back to the maximum value when the light is turned on

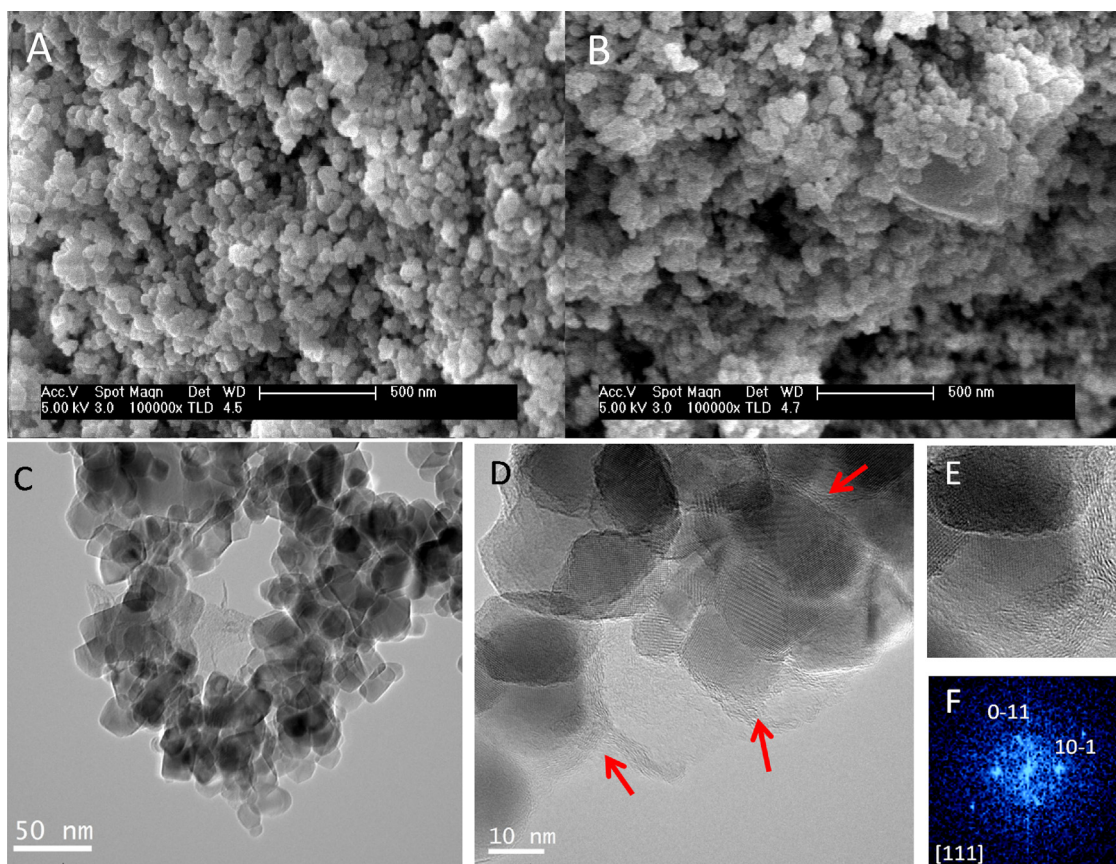


Fig. 3. SEM images of P25-rGO 0% (A) and P25-rGO 0.5% (B). TEM and HRTEM images of P25-rGO 1% (C and D): High magnification of P25-rGO 1% showing the presence of rGO layers (E). Fast Fourier Transform (FFT) of the photocatalyst.

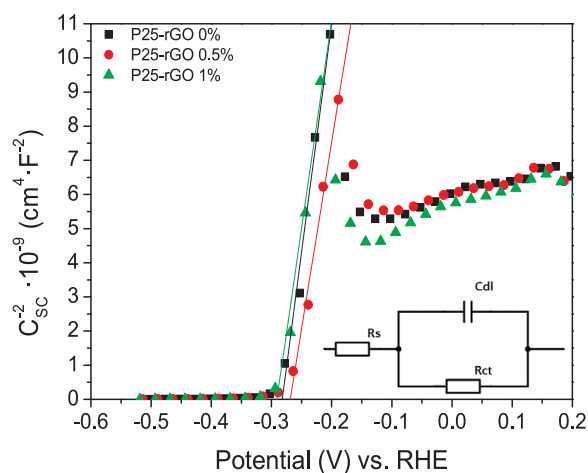


Fig. 4. Mott-Schottky plots of P25-rGO 0%, P25-rGO 0.5% and P25-rGO 1% electrodes. The intercept of the linear regime with the x-axis determines the flat-band potential. The equivalent Randles circuit is inseted.

again, showing a good reproducibility of the different cycles. When the samples were irradiated with UV–vis irradiation (Fig. 5A) the photocurrent values obtained for P25-rGO 1% and P25-rGO 0.5% were around $6.5 \mu\text{A cm}^{-2}$ and $3.75 \mu\text{A cm}^{-2}$ respectively, being 10 and 6 times higher than those values obtained for P25-rGO 0%. This effect in the photocurrent cycles could be attributed to the rGO /TiO₂ coupling which allows a faster transfer of the photogenerated electrons from the conduction band of TiO₂ to rGO and further transfer to the electrode. When the films were irradiated with visible light (Fig. 5B) the photocurrent response followed the same sequence. However, photocurrent values

less than 1% were reached when irradiating with wavelength higher than 450 nm. In both figures, a slow photocurrent response of P25-rGO 0% could be ascribed to the electrons trapped in trapping sites such as Ti^{3+} . The photogenerated electrons are first trapped in surface or shallow bulk trap sites and further migrate to deeper states, becoming less mobile [5,34]. Therefore, while the “trap filling” process is taking place, only part of the photogenerated electrons can be transferred to the FTO leading to the slow increase of the photocurrent response [35]. The slow photocurrent fall when the light was turned off could be the result of stored electrons in rGO being released gradually [7]. To sum up, the photocurrents results reveal that more effective charge separations of the photogenerated electron-hole pairs were attained with rGO modified TiO₂. This is mainly due to the higher conductance values when rGO was present, which enables a faster charge carrier transfer between the film and the electrode [26,33].

Electrochemical impedance spectroscopy (EIS) was carried out to obtain the respective Nyquist plots (Fig. 6). From these graphs, information about the electron-transfer process across the semiconductor-electrolyte interface can be obtained. It can be noted that the greater the amount of rGO mass concentration, the smaller the semicircle radius, which indicates a more efficient charge separation and lower interfacial charge transfer resistance [7,25,36]. A more detailed explanation related to this conclusion is included in the Supplementary Information: Nyquist plot explanation.

In most photocatalytic applications the only electron acceptor available is oxygen. Therefore, the reduction process of oxygen by the photogenerated electrons is crucial. The formation of superoxide anion radicals ($\text{O}_2^{\cdot-}$) and hydrogen peroxide (H_2O_2) by oxygen reduction by one or more electrons is especially important when the photocatalysts are irradiated by visible light, as previously reported in water disinfection [10,37]. The different oxygen reduction reactions depending on

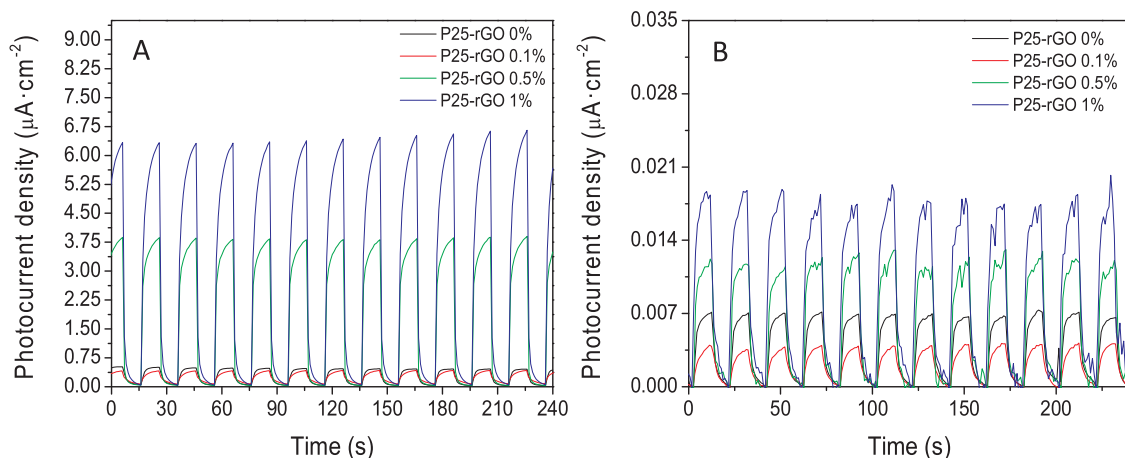


Fig. 5. Photocurrent density versus time curves for the hybrid materials with different rGO mass doping ratio under (A) chopped UV-vis light and (B) chopped visible light ($\lambda > 450$ nm).

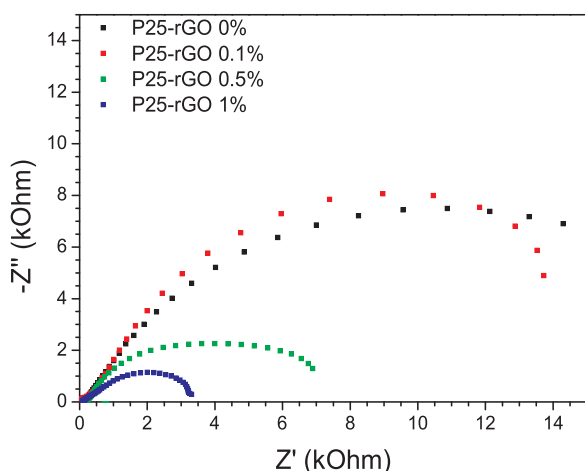
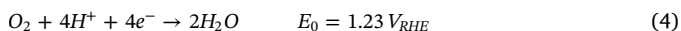
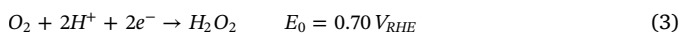
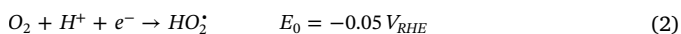


Fig. 6. Nyquist plots measured in 0.1 M Na_2SO_4 aqueous solution under 0 V bias vs. RHE. The employed frequency range was from 0.1 Hz to 30 kHz.

the number of electrons involved and their respective reduction potentials are shown below [8,38]:



Linear sweep voltammetry experiments were performed to measure the oxygen reduction currents and thus analyze the effect of rGO coupling with TiO_2 on the reduction mechanism of oxygen (Fig. 7).

The unmodified TiO_2 exhibited a negligible oxygen reduction current at potentials above 0 V vs. RHE ($< 3 \mu\text{A cm}^{-2}$), pointing out that a slow reduction process occurred. On the other hand, when titanium dioxide was modified by rGO, a significant rise of the oxygen reduction current was detected up to 0.4 V vs. RHE. The reduction current values obtained at 0 V vs. RHE for P25-rGO 1% ($> 23 \mu\text{A cm}^{-2}$) and P25-rGO 0.5% ($< 12 \mu\text{A cm}^{-2}$) were nearly 10 and 5 times higher than the value reached by P25-rGO 0% ($2.4 \mu\text{A cm}^{-2}$). In conclusion, the higher the amount of rGO in the nanocomposite, the larger the increase of the reduction current, probably because of the lower charge transfer resistance of these photocatalysts.

3.2. Photocatalytic activity of P25-rGO composites

To investigate the photocatalytic activity of P25-rGO 0% and P25

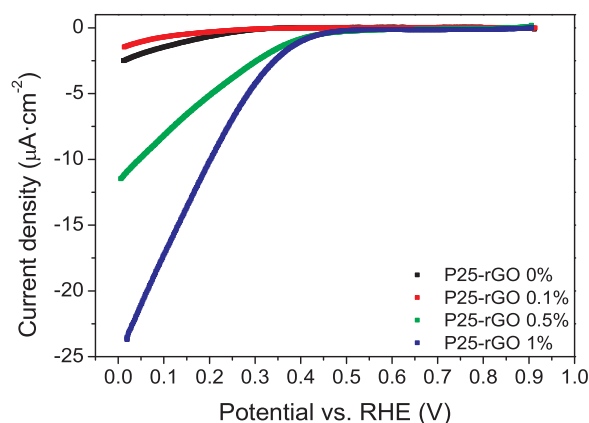


Fig. 7. Oxygen reduction current vs. applied potential for the different modified TiO_2 .

modified with rGO, the degradation of 1 mM oxalic acid aqueous solution under UV-A irradiation was followed using ATR-FTIR. In situ ATR-FTIR is a useful technique to characterize the adsorbed species on the photocatalyst surface and monitoring the photodegradation of the surface complexes and intermediates adsorbed [23,39–41]. Oxalic acid was chosen since it is a model compound which is usually generated as an intermediate during the degradation of more complex pollutants, e.g. phenolic compounds, and because of its simple oxidation pathway [23,39]. Oxalic acid is transformed into CO_2 and the process can be monitored in an easy way since few intermediates (formic acid or carbonates) are formed [39,41].

Firstly, measurements were carried out to follow the adsorption process for 45 min. Fig. S2 shows the time evolution of the recorded spectra of adsorbed oxalic acid in the dark (the time interval between every spectra was 5 min). Several studies have previously shown the main features of FTIR spectrum of oxalic acid adsorbed on TiO_2 [39,40]. In brief, the band between 1800 and 1600 cm^{-1} and the shoulder at 1590 cm^{-1} were assigned to $\text{C}=\text{O}$ symmetric stretching mode and $\text{O}-\text{C}=\text{O}$ asymmetric stretching mode. In the region between 1500 and 1200 cm^{-1} two bands could easily be differentiated at around 1420 and 1300 cm^{-1} . The first band could be ascribed to the symmetric stretching mode of $\text{C}-\text{O}$, $\text{C}-\text{C}$, and $\text{O}-\text{C}=\text{O}$ bonds, whereas the second peak rise as a consequence of symmetric stretching mode of $\text{C}-\text{O}$ bonds overlapping with the bending mode of the $\text{O}-\text{C}=\text{O}$ bonds. A shoulder close to the peak observed at 1300 cm^{-1} has also been related to outer sphere complexes in the case of rutile [40]. By looking at the time evolution of the recorded spectra it could be noticed that the

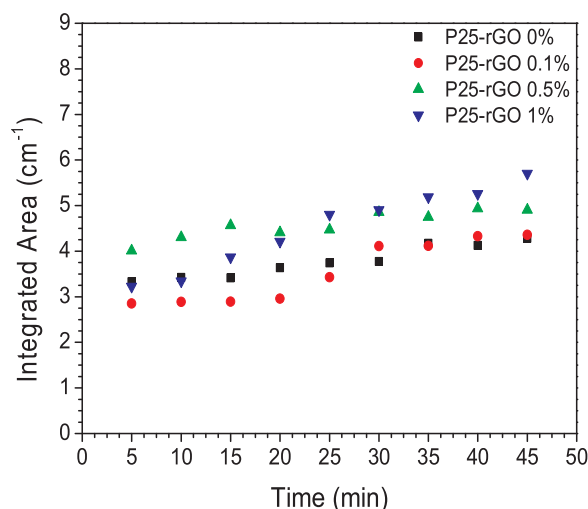


Fig. 8. Time evolution of the integrated IR spectral signals between 1200 and 1800 cm^{-1} of the films in contact with 3 mL of oxalic acid solution in the dark.

oxalic acid has been mostly adsorbed during the first five minutes, regardless of the nanocomposite. Afterwards, only a slight increase of the intensity was detected, especially, the intensity of the shoulder between 1620 and 1580 cm^{-1} changes slightly, and the equilibrium appeared to be reached after 25 min. The evolution of the integrated area of the peaks between 1800 and 1200 cm^{-1} as a function of time is depicted in Fig. 8. Only slight changes of the integrated area corresponding to adsorbed oxalic acid was detected after the high value was obtained at 5 min. All the curves from the integrated spectra revealed a behavior similar to a Langmuir adsorption isotherm [40], despite the fact that the titanium dioxide was modified with rGO. Comparing the values of the integrated area reached by the studied photocatalysts a rise of the amount of adsorbed oxalic acid was detected when the rGO concentration in the TiO_2 increased. This result may be attributed to the high surface area and high selectivity exhibited by rGO [42,43].

Subsequent to the adsorption process of oxalic acid on the photocatalyst surface, a series of spectra were recorded to track the oxalic acid degradation when the sample was irradiated by 365 nm light with an intensity of 1.0 mW cm^{-2} for 2 h. The time evolution of the recorded spectra of the adsorbed organic compound during illumination with UV-A light is displayed in Fig. S.3. Following the first spectrum a decrease of the intensity in the wavenumber region between 1620 and 1550 cm^{-1} was observed. This is related to removal of the least stable surface complex that represents the adsorption of oxalate [23,40]. On the other hand, the peak at 1300 cm^{-1} barely suffered any changes under irradiation.

To better compare these results, the area under the peaks in the region between 1800 and 1200 cm^{-1} was estimated for the spectra recorded every 5 min (Fig. 9). A pseudo-first order kinetic was observed for the oxalate surface photodegradation reaction. The obtained pseudo-first order rate constants were $5.2 \cdot 10^{-3} \pm 2.3 \cdot 10^{-4}$, $5.5 \cdot 10^{-3} \pm 2.1 \cdot 10^{-4}$, $5.7 \cdot 10^{-3} \pm 1.2 \cdot 10^{-4}$ and $6.8 \cdot 10^{-3} \pm 1.7 \cdot 10^{-4} \text{ min}^{-1}$ for P25-rGO 0%, P25-rGO 0.1%, P25-rGO 0.5%, and P25-rGO 1%, respectively. The modified TiO_2 with 0.5% and 1% yielded slightly higher values of the pseudo-first order kinetic constant than pure TiO_2 (1.1 and 1.3 times higher respectively). This slight rise could be attributed to the higher adsorption capacity as a result of the introduction of rGO, previously mentioned above, and the more efficient separation of the photogenerated charge carriers according to the electrochemical characterization.

To further investigate the photocatalytic degradation of oxalic acid, reactions in which the photocatalysts were suspended in a 1 mM oxalic acid aqueous solution were conducted. UV-A light with an intensity of 1.08 mW cm^{-2} was used to irradiate the reactor. No photolysis of oxalic

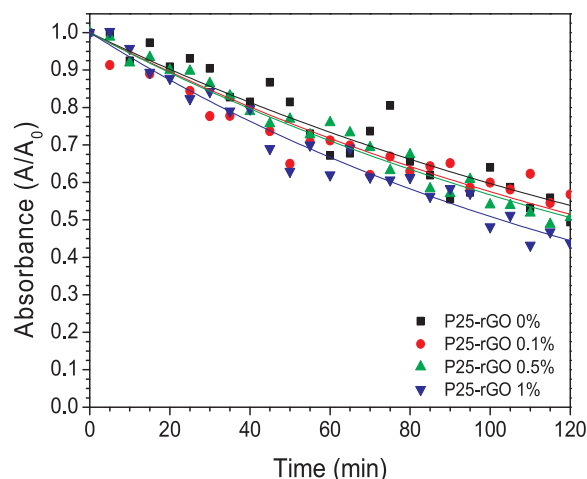


Fig. 9. Time evolution of the integrated area between 1800 and 1200 cm^{-1} . A 365 nm LED with an intensity of 1 mW cm^{-2} was used to illuminate the sample.

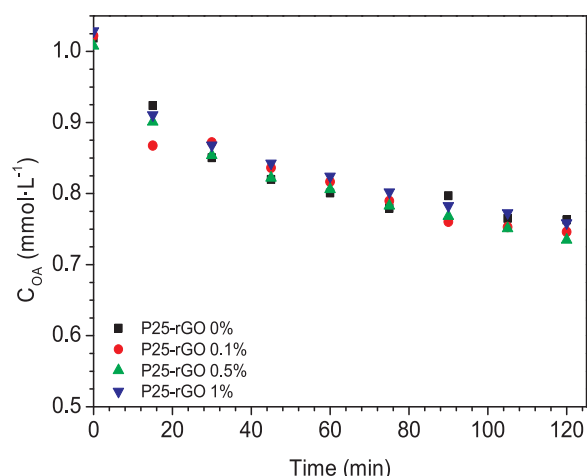


Fig. 10. Time evolution of the concentration of oxalic acid using P25-rGO 0%, P25-rGO 0.1%, P25-rGO 0.5% and P25-rGO 1%. The sample were irradiated with UV-A light with an intensity of 1.08 mW cm^{-2} .

acid was previously reported [44,45]. The photocatalytic degradation of oxalic acid over different studied photocatalysts is shown in Fig. 10 as the plot of the oxalic acid concentration versus illumination time. In this case, even smaller differences were observed in the photocatalytic degradation curves obtained for the nanocomposites compared to the studies using ATR-FTIR spectroscopy. One of the advantages of characterizing the photocatalytic oxidation using the ATR-FTIR technique is that differences of the effective path lengths are diminished as a thin layer is deposited on the ATR crystal. However, when the photocatalyst is suspended in the reaction medium, light-block effects occur. For instance, an excess of rGO can block the amount of light reaching the TiO_2 nanoparticles [25], leading to lower photonic efficiencies in spite of the other beneficial properties of rGO. That might be the reason why P25-rGO 0.5% yielded the highest photodegradation in suspension, even though the surface photocatalytic reaction was faster for P25-rGO 1% as was shown by the ATR-FTIR experiments. Furthermore, an excessive amount of rGO could lead to the formation of clusters or agglomerates acting as recombination centers [25,46].

Despite the fact that the electrochemical characterization indicated that the modification of TiO_2 with rGO led to much more efficient separation of the photogenerated charge carriers, similar photodegradation kinetics were observed for the different photocatalysts used in this study. In order to evaluate the effect of the mass doping ratio of rGO on the role played by the photogenerated electrons and holes and their

influence in the photocatalytic mechanism under UV light, EPR measurements were performed to detect the reactive oxygen species (ROS) involved in the photocatalytic process. Dissolved molecular oxygen plays a crucial role since it reacts with trapped electrons, subsequent to being photogenerated, forming superoxide anion radicals ($O_2^{\cdot-}$) [37]. The generation of $O_2^{\cdot-}$ was detected at room temperature by performing spin trapping technique using DMPO. The photocatalysts were suspended in DMSO instead of water to avoid the facile disproportionation of the superoxide radical that leads to a slow reaction between superoxide anion radicals or hydroperoxyl radicals and DMPO [47]. Moreover, using DMSO as a solvent favors the generation and trapping of $O_2^{\cdot-}$ because of the stabilization effect of the aprotic solvent and the higher solubility of molecular oxygen [48]. Fig. S4 displays EPR spectra obtained at different irradiation times of the P25-rGO suspensions saturated with O_2 . Under these conditions, for all the studied photocatalysts, a series of peaks were observed immediately after irradiation at around 337 mT and 340.5 mT for example. Then they decayed at the same time the intensity of other peaks at 336.5 mT and 338 mT increased. The simulation analysis of the EPR spectra (Fig. S5) revealed that the interaction of EPR signals could be ascribed to a combination of $DMPO-O_2^{\cdot-}$ ($a_N = 1.282$ mT, $a_H^\beta = 1.035$ mT, $a_H^\gamma = 0.132$ mT; $g = 2.0058$) and $DMPO-CH_3$ ($a_N = 1.462$ mT, $a_H^\beta = 2.093$ mT; $g = 2.0057$) [48,49], where the two first signals mentioned above were attributed to the $DMPO-O_2^{\cdot-}$ whereas the peaks at 336.5 mT and 338 mT corresponded to the generation of $DMPO-CH_3$. The formation of CH_3^{\cdot} was previously reported as the result of the oxidation of DMSO by HO^{\cdot} radicals generated by the presence of adsorbed water onto the catalyst surface [48,50].

To delay the generation of $DMPO-CH_3$ and achieve a better comparison of the ability to generate $O_2^{\cdot-}$ radicals, the samples were irradiated for just two seconds, and afterwards, the EPR spectra was recorded (Fig. S6). The simulation confirmed the generation of $DMPO-O_2^{\cdot-}$, characterized by hyperfine splitting $a_N = 1.282$ mT, $a_H^\beta = 1.035$ mT, $a_H^\gamma = 0.132$ mT; $g = 2.0058$ [48,49]. Although the differences between these spectra are small, P25-rGO 0.1 and 0.5% exhibit a higher intensity. These results were attributed to the ability to reduce oxygen more easily when the TiO_2 was modified by rGO, Fig. 7.

Valence band holes react with adsorbed hydroxide anions and water molecules giving rise to hydroxyl radicals, which together with holes are crucial oxidative species in the photocatalytic oxidation of dissolved organic matter [48]. Furthermore, hydroxyl radicals can be formed by consecutive reactions of photogenerated $O_2^{\cdot-}$ with protons from the aqueous solution (reactions (4)–(7)):



The detection of hydroxyl radicals was performed upon irradiation of P25-rGO in O_2 and N_2 saturated aqueous suspensions at room temperature (Fig. S7). No signal was measured in the dark for any of the photocatalysts. However, when the sample was irradiated by a Xe lamp, a four-line EPR signal was identified. The simulation analysis, Fig. S8, confirmed the generation of $DMPO-HO^{\cdot}$ ($a_N = 1.497$ mT, $a_H = 1.477$ mT; $g = 2.0057$) [48,49].

It can be noticed that the experimental spectra perfectly corresponded with the simulated one. The signal appeared immediately after exciting the sample and suffered a decreased in intensity after 30 s (Fig. S7). No significant differences were observed among the spectra obtained for the studied photocatalysts, which indicates that a similar concentration of hydroxyl radicals were photogenerated in the presence of rGO. In order to discuss more easily the generation of reactive oxygen species in EPR experiments, the area of the EPR spectra signals, obtained under the different atmospheres, were calculated and plotted

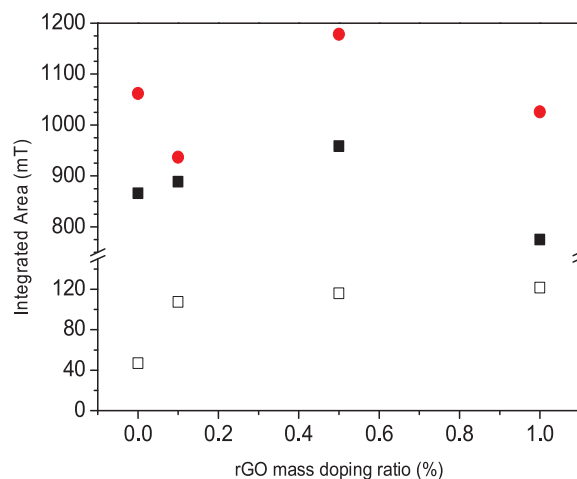


Fig. 11. Calculated area for $DMPO-OH$ adduct in O_2 (■), $DMPO-O_2^{\cdot-}$ adduct in O_2 (●), $DMPO-OH$ adduct in N_2 (□) for the studied P25-rGO photocatalysts. The area of the $DMPO-OH$ and $DMPO-O_2^{\cdot-}$ adducts were calculated from the EPR spectra obtained after illuminating for 30 and 2 s respectively.

versus rGO mass concentration (Fig. 11). Similar values for $DMPO-HO^{\cdot}$ and $DMPO-O_2^{\cdot-}$ were found regardless of the rGO doping ratio in O_2 saturated suspensions, with P25-rGO 0.5% yielding the highest integrated area for both measured reactive oxygen species, $O_2^{\cdot-}$ and HO^{\cdot} . The slight increase detected for some of these nanocomposites could be ascribed to the most effective separation of photogenerated charge carriers and the ability to achieve a more efficient reduction of oxygen. Regarding P25-rGO 1%, the integrated area values decreased as a result of the shielding effect caused by an excess of rGO that could also imply the formation of clusters acting as recombination centers [15,46], as was already pointed out in the above discussion about oxalic acid photodegradation. However, when the $DMPO-HO^{\cdot}$ EPR spectra measured in N_2 saturated suspensions was integrated, the integrated area was found to increase three times when 0.1% rGO was incorporated to TiO_2 . Higher rGO concentrations only led to a slight increase. These results evinced the role played by rGO as an electron acceptor which enables the reaction between holes and adsorbed water to generate hydroxyl radicals whereas the electrons are dragged to rGO.

Even though electrochemical results indicated a great enhancement in separating electron-hole pairs, only a small improvement of photocatalytic activity was found in oxalic acid experiments and in ROS detection. To better understand of the processes occurring upon illumination transient absorption spectroscopy (TAS) has been conducted in the microsecond scale, which allows studying the reaction dynamics of the photogenerated charges. The TAS decays for the TiO_2 and TiO_2 -rGO powders under N_2 or O_2 were obtained after exciting the sample with laser pulses of light with a wavelength of 355 nm and energy of 2.2 mJ cm^{-2} per pulse (Fig. 12). Probe wavelengths at 400 nm and 660 nm were used to follow the decay kinetics of the trapped holes and electrons, respectively [5,51–55].

A kinetic model based on fractal surfaces [21] was applied to evaluate the effect of rGO and the atmosphere on the charge carriers dynamics:

$$\Delta J = \frac{A(1-h)}{(1-h) + Ak_f t^{1-h}} \quad (9)$$

Where $k_f t^{-h}$ represents a rate coefficient and a time dependent factor, h is related to the fractal dimension of the surface and A represents the height of the transient signal. The k_f and A parameters are shown in Table 1.

Since rGO acts as an electron acceptor, electrons are transferred from TiO_2 to rGO in the ps time regime [5,55]. That's why the A

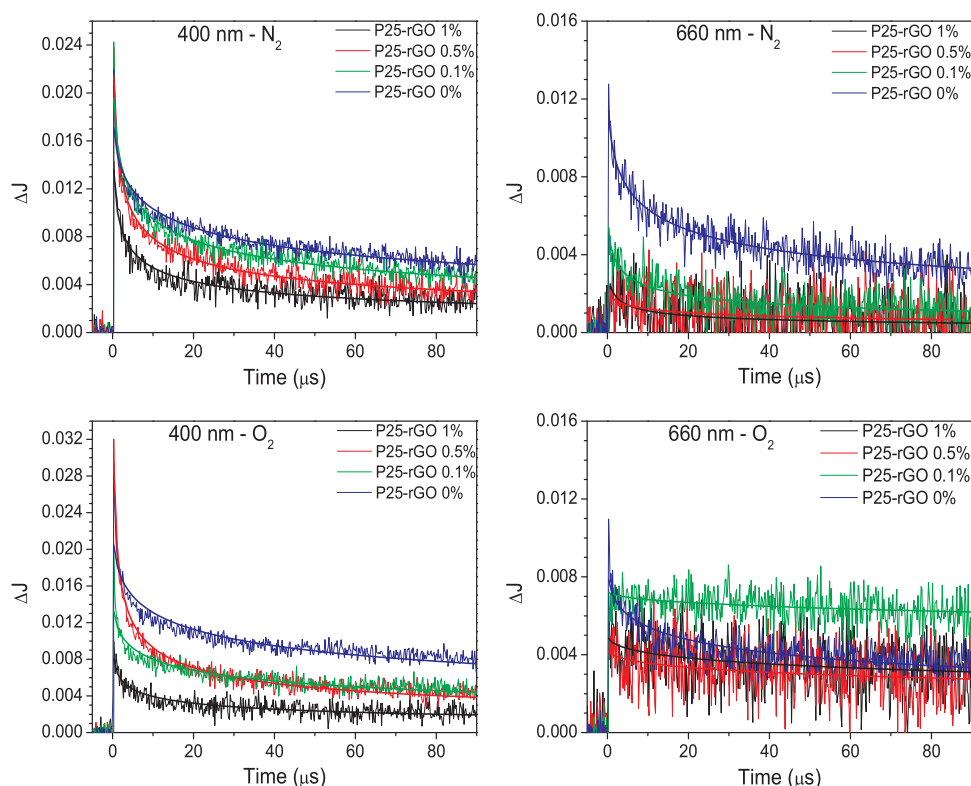


Fig. 12. Time profiles of transient absorption at 400 nm and 660 nm of P25-rGO 0%, P25-rGO 0.1%, P25-rGO 0.5% and P25-rGO 1% under a N_2 and O_2 atmosphere.

parameters and the initial signals from trapped electrons (660 nm), observed in Table 1 and Fig. 12, were less intense compared to bare TiO_2 in both atmospheres. It seems that 0.5% is the optimal rGO mass doping ratio because a higher addition of rGO does not mean a further reduction of the initial transient absorption signal. It is noteworthy that in O_2 atmosphere the initial intensity obtained by bare TiO_2 at 660 nm was lower than that obtained in N_2 atmosphere. On the other hand, the initial height of the P25-rGO photocatalysts rose compared to the intensity observed in N_2 atmosphere. The lowest initial intensity at 660 nm in O_2 was observed for P25-rGO 0.5% indicating that a more electrons were transferred either to rGO or to O_2 . All in all, the initial intensity difference between bare TiO_2 and P25 modified with rGO, and therefore the electron transfer, was considerable decreased in the presence of O_2 . These results agreed with the EPR results. Whereas low differences in $DMPO-O_2^{\cdot-}$ and $DMPO-HO^{\cdot}$ areas were noted in the presence of O_2 , with P25-rGO 0.5% yielding the best results, the $DMPO-HO^{\cdot}$ areas measured for the TiO_2 -rGO nanocomposites was much higher than that obtained for P25-rGO 0% in N_2 atmosphere.

As for the rate coefficients, k_f values estimated from the TAS decays in N_2 atmosphere increased with the rGO content becoming between four and ten times higher than those for P25-rGO 0%. In TAS studies carried out in the μs time scale, the recombination between trapped electrons and holes was observed [5]. Thus, results indicates that in N_2

atmosphere, where electrons cannot be released, rGO acts as a recombination center that leads to a faster charge carrier recombination rate [55]. On the other hand, in O_2 atmosphere k_f values were reduced when rGO was added to TiO_2 . Hence, the charge carrier recombination rate was decreased, and thus it could lead to higher $O_2^{\cdot-}$ generation rate.

Concerning the 400 nm signal, it could be ascribed to deeply trapped holes that does not affect the photocatalytic activity [55]. This was verified since only small differences in the initial intensity were observed when rGO was added. In the presence of O_2 , the initial height of the signal increased, due to the presence of an electron scavenger that reduced the recombination rate. Apart from that, the decay constants k_f increased with the addition of rGO and were similar in both atmospheres. However, it was previously corroborated that the charge carrier recombination rate was decreased in the presence of O_2 . Hence, the decay rates observed at 400 nm was attributed to the migration of holes between different trapping sites (after electrons were transferred from TiO_2 to rGO) [55].

To sum up, the presence of O_2 hinders the transfer of free electrons from TiO_2 to rGO but favors the electron transfer from bare TiO_2 . In other words, the role of rGO as an electron acceptor is less significant in O_2 atmosphere. As a consequence, lower differences in the $O_2^{\cdot-}$ and HO^{\cdot} generation between bare TiO_2 and P25-rGO photocatalysts were

Table 1

Estimated kinetic parameters of the transient decay signals dependent on the rGO (%) mass concentration and initial transient absorption obtained under N_2 and O_2 atmospheres.

	N2 — 400 nm		N2 — 660 nm		O2 — 400 nm		O2 — 660 nm	
	k_f (au μs -1) $\cdot 10^{-3}$	A $\cdot 10^2$	k_f (au μs -1) $\cdot 10^{-3}$	A $\cdot 10^2$	k_f (au μs -1) $\cdot 10^{-3}$	A $\cdot 10^2$	k_f (au μs -1) $\cdot 10^{-3}$	A $\cdot 10^2$
P25-rGO 0%	2.43	2.25	5.56	1.50	2.18	2.47	4.47	0.91
P25-rGO 0.1%	3.41	3.12	18.53	0.85	3.91	1.65	0.58	0.73
P25-rGO 0.5%	5.00	5.09	26.90	0.26	5.78	7.75	3.19	0.44
P25-rGO 1%	6.91	2.78	44.32	0.60	10.17	1.15	2.95	0.51

detected.

4. Conclusions

TiO₂-rGO photocatalysts were successively prepared by a hydrothermal method. The junction between TiO₂ and rGO involved a higher disorder degree as a consequence of the strong interaction between TiO₂ and rGO sheets. However, it did not mean a change of the surface area or the XRD patterns. Besides, the optical band gap and the conduction and valence band potentials were unchanged by the modification of TiO₂ with rGO, measuring values around -0.38 and 2.75 V vs. RHE, respectively. Electrochemical impedance spectroscopy (EIS) and photocurrent response measurements were carried out to evaluate the efficiency of charge separation. The addition of rGO led to a low charge transfer resistance across the electrode-electrolyte interface and even a tenfold increase in the photocurrent values was observed for P25-rGO 1%, indicating a more efficiency in the electron-hole separation.

A higher oxygen reduction current was found when increasing the rGO concentration. This could lead to an enhancement of the generation of reactive oxygen species (ROS). However, in the oxalic acid degradation only small differences were observed. Concerning the surface reaction measured using the ATR-FTIR technique, the higher the amount of rGO added, the higher the adsorption. As a consequence the surface reaction was faster for P25-rGO 1% thanks to a more efficient reduction of oxygen and lower charge transfer resistance, which suggests that this hybrid nanocomposite was also less limited by possible O₂ mass transfer limitations. Under slurry photoreactor conditions at oxygen excess, the oxalic acid photo-oxidation evolution was similar for all the studied catalysts. The EPR experiments revealed that only a slight increase of the generated HO[•] and O₂^{•-} for P25-rGO 0.5% as a result of slightly lower decay kinetics of the photogenerated electrons found in the TAS studies. On the other hand, regarding generation of HO[•] by N₂ saturated suspensions, the addition of only 0.1% rGO mass concentration was enough to detect a threefold increase of the EPR signal related to DMPO–HO[•]. Finally, to relate photocatalytic activity and EPR studies, the role played by rGO was investigated by conducting transient absorption spectroscopy (TAS) experiments under O₂ and N₂ atmospheres. TAS decay kinetics corroborated that rGO acts as an electron acceptor, occurring the electron transfer from TiO₂ to rGO in the ps time scale. This explained the higher DMPO–HO[•] signal obtained in N₂ atmosphere when rGO was added. However, the role played by rGO was not crucial in excess of dissolved O₂, which meant lower differences in the O₂^{•-} and HO[•] generation detected by EPR between bare TiO₂ and TiO₂ modified with rGO.

Acknowledgements

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi: <https://doi.org/10.1016/j.apcatb.2018.09.070>.

References

- [1] S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Gernjak, *Catal. Today* 147 (2009) 1–59.
- [2] P. Fernández-Ibáñez, M.I. Polo-López, S. Malato, S. Wadhwa, J.W.J. Hamilton, P.S.M. Dunlop, R. D'Sa, E. Magee, K. O'Shea, D.D. Dionysiou, J.A. Byrne, *Chem. Eng. J.* 261 (2015) 36–44.
- [3] J. Carbajo, P. García-Muñoz, A. Tolosana-Moranchel, M. Faraldos, A. Bahamonde, *Environ. Sci. Pollut. Res.* (2014) 12233–12240.
- [4] M. Martín-Sómer, B. Vega, C. Pablos, R. van Grieken, J. Marugán, *Appl. Catal. B: Environ.* 221 (2018) 258–265.
- [5] J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, D.W. Bahnemann, *Chem. Rev.* 114 (2014) 9919–9986.
- [6] P. Ribao, M.J. Rivero, I. Ortiz, *Environ. Sci. Pollut. Res.* 24 (2017) 12628–12637.
- [7] T. Liu, B. Liu, L. Yang, X. Ma, H. Li, S. Yin, T. Sato, T. Sekino, Y. Wang, *Appl. Catal. B: Environ.* 204 (2017) 593–601.
- [8] J.Z. Bloh, R. Dillert, D.W. Bahnemann, *Phys. Chem. Chem. Phys.* 16 (2014) 5833–5845.
- [9] M. Minella, M. Demontis, M. Sarro, F. Sordello, P. Calza, C. Minero, *J. Mater. Sci.* 50 (2015) 2399–2409.
- [10] L.L. Tan, S.P. Chai, A.R. Mohamed, *ChemSusChem* 5 (2012) 1868–1882.
- [11] M. Faraldos, A. Bahamonde, *Catal. Today* 285 (2017) 13–28.
- [12] N. Zhang, M.-Q. Yang, S. Liu, Y. Sun, Y.-J. Xu, *Chem. Rev.* 115 (2015) 10307–10377.
- [13] C. Han, N. Zhang, Y.-J. Xu, *Nano Today* 11 (2016) 351–372.
- [14] K.-Q. Lu, Y. Chen, X. Xin, Y.-J. Xu, *Appl. Catal. B: Environ.* 224 (2018) 424–432.
- [15] M. Minella, F. Sordello, C. Minero, *Catal. Today* 281 (2017) 29–37.
- [16] H.N.D. Zhebo Chen, Eric Miller, *Photoelectrochemical Water Splitting Standards, Experimental Methods, and Protocols*, Springer, New York, 2013.
- [17] M. Cao, P. Wang, Y. Ao, C. Wang, J. Hou, J. Qian, *Chem. Eng. J.* 264 (2015) 113–124.
- [18] L.L. Tan, W.J. Ong, S.P. Chai, A.R. Mohamed, *Chem. Eng. J.* 283 (2016) 1254–1263.
- [19] R.L.Z.R. Jenkins, *Introduction to X-Ray Powder Diffractometry*, John Wiley & Sons Inc., New York, 1996.
- [20] R.A. Spurr, H. Myers, *Anal. Chem.* 29 (1957) 760–762.
- [21] F. Seland, J. Schneider, D.W. Bahnemann, *J. Phys. Chem. C* (2017).
- [22] S. Ito, T.N. Murakami, P. Comte, P. Liska, C. Grätzel, M.K. Nazeeruddin, M. Grätzel, *Thin Solid Films* 516 (2008) 4613–4619.
- [23] C.B. Mendive, D.W. Bahnemann, M.A. Blesa, *Catal. Today* 101 (2005) 237–244.
- [24] H. Belhadj, S. Melchers, P.K.J. Robertson, D.W. Bahnemann, *J. Catal.* 344 (2016) 831–840.
- [25] A. Morais, C. Longo, J.R. Araujo, M. Barroso, J.R. Durrant, A.F. Nogueira, *Phys. Chem. Chem. Phys.* 18 (2016) 2608–2616.
- [26] N.J. Bell, Y.H. Ng, A. Du, H. Coster, S.C. Smith, R. Amal, *J. Phys. Chem. C* 115 (2011) 6004–6009.
- [27] A.W. Morawski, E. Kusiak-Nejman, A. Wanag, J. Kapica-Kozar, R.J. Wróbel, B. Ohtani, M. Aksienionek, L. Lipińska, *Catal. Today* 280 (2017) 108–113.
- [28] S. Kaniyankandy, S.N. Achary, S. Rawalekar, H.N. Ghosh, *J. Phys. Chem. C* 115 (2011) 19110–19116.
- [29] W. Fan, Q. Lai, Q. Zhang, Y. Wang, *J. Phys. Chem. C* 115 (2011) 10694–10701.
- [30] E. Gao, W. Wang, M. Shang, J. Xu, *J. Chem. Soc. Faraday Trans. 13* (2011) 2887–2893.
- [31] S. Huang, Q. He, J. Zai, M. Wang, X. Li, B. Li, X. Qian, *Chem. Commun.* 51 (2015) 8950–8953.
- [32] H. Yang, J. Tian, T. Li, H. Cui, *Catal. Commun.* 87 (2016) 82–85.
- [33] C. Wang, M. Cao, P. Wang, Y. Ao, J. Hou, J. Qian, *Appl. Catal. A: Gen.* 473 (2014) 83–89.
- [34] Y. Tamaki, A. Furube, M. Murai, K. Hara, R. Katoh, M. Tachiya, *Phys. Chem. Chem. Phys.* 9 (2007) 1453–1460.
- [35] J. Yu, G. Dai, B. Huang, *J. Phys. Chem. C* 113 (2009) 16394–16401.
- [36] Q. Wang, N. Zhu, E. Liu, C. Zhang, J.C. Crittenden, Y. Zhang, Y. Cong, *Appl. Catal. B: Environ.* 205 (2017) 347–356.
- [37] B.R. Cruz-Ortiz, J.W.J. Hamilton, C. Pablos, L. Díaz-Jiménez, D.A. Cortés-Hernández, P.K. Sharma, M. Castro-Alferez, P. Fernández-Ibáñez, P.S.M. Dunlop, J.A. Byrne, *Chem. Eng. J.* 316 (2017) 179–186.
- [38] H. Mattila, S. Khorobrykh, V. Havurinne, E. Tyystjärvi, *Journal of photochemistry and photobiology B: biology* 152, Part B (2015) 176–214.
- [39] C.B. Mendive, T. Bredow, M.A. Blesa, D.W. Bahnemann, *Phys. Chem. Chem. Phys.* 8 (2006) 3232–3247.
- [40] C.B. Mendive, T. Bredow, A. Feldhoff, M.A. Blesa, D. Bahnemann, *Phys. Chemistry Chem. Phys.* 11 (2009) 1794–1808.
- [41] C.B. Mendive, T. Bredow, J. Schneider, M. Blesa, D. Bahnemann, *J. Catal.* 322 (2015) 60–72.
- [42] H. Adamu, P. Dubey, J.A. Anderson, *Chem. Eng. J.* 284 (2016) 380–388.
- [43] H. Zhang, X. Lv, Y. Li, Y. Wang, J. Li, *ACS Nano* 4 (2009) 380–386.
- [44] V. Iliev, D. Tomova, L. Bilyarska, A. Eliyas, L. Petrov, *Appl. Catal. B: Environ.* 63 (2006) 266–271.
- [45] V. Iliev, D. Tomova, S. Rakovsky, A. Eliyas, G.L. Puma, *J. Mol. Catal. A Chem.* 327 (2010) 51–57.
- [46] J.Z. Bloh, R. Dillert, D.W. Bahnemann, *J. Phys. Chem. C* 116 (2012) 25558–25562.
- [47] G. Liu, J. Zhao, H. Hidaka, *J. Photochem. Photobiol. A: Chem.* 133 (2000) 83–88.
- [48] D. Dvoranová, Z. Barbieriková, V. Brezová, *Molecules* 19 (2014) 17279.
- [49] G.R. Buechner, *Free Radic. Biol. Med.* 3 (1987) 259–303.
- [50] V. Brezová, S. Gabčová, D. Dvoranová, A. Staško, *J. Photochem. Photobiol. B, Biol.* 79 (2005) 121–134.
- [51] D.W. Bahnemann, M. Hilgendorff, R. Memming, *J. Phys. Chem. B* 101 (1997) 4265–4275.
- [52] A. Furube, T. Asahi, H. Masuhara, H. Yamashita, M. Anpo, *J. Phys. Chem. B* 103 (1999) 3120–3127.
- [53] Y. Tamaki, A. Furube, R. Katoh, M. Murai, K. Hara, H. Arakawa, M. Tachiya, *Comptes Rendus Chim.* 9 (2006) 268–274.
- [54] T. Yoshihara, R. Katoh, A. Furube, Y. Tamaki, M. Murai, K. Hara, S. Murata, H. Arakawa, M. Tachiya, *J. Phys. Chem. B* 108 (2004) 3817–3823.
- [55] A.O.T. Patrocínio, J. Schneider, M.D. Franca, L.M. Santos, B.P. Caixeta, A.E.H. Machado, D.W. Bahnemann, *RSC Adv.* 5 (2015) 70536–70545.